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13. ABSTRACT (Maximum 200 words)  Report developed under SBIR contract. There is a great need to develop a real-time analytical technique for monitoring trace vapor emissions during open burning/open detonation (OB/OD) testing in BangBox facilities. In Phase I of this study, a corona discharge atmospheric pressure ionization/time-of-flight mass spectrometer CDAPI/TOFMS was successfully developed and evaluated for analyzing permanent gas, volatile organic, semi-volatile organic, and toxic metal target analytes selected from previous OB/OD tests. Mass spectra illustrating selectivities were obtained. Sensitivities in the <b>parts-per-trillion</b> range and calibration curves were determined for various analytes. The CDAPI/TOFMS was shown to be more sensitive than GC/MS, SFC/MS, and FTIR. A detailed design of a prototype CDAPI/TOFMS for construction and testing during Phase II of this project was produced. The new design emphasizes improved instrument performance and facilitates instrument manufacturing and commercialization. <b>All Phase I objectives were accomplished.</b>  Successful development of the proposed technology will significantly reduce the time and cost of obtaining OB/OD vapor emission data, and provide instrumentation for monitoring alternative methods such as incineration. The technology also has application to explosives and drug detection. Commercial applications include monitoring of workplace air environments, sniffing of hazardous waste sites, and monitoring of chemical process streams.				
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**SMALL BUSINESS INNOVATION RESEARCH (SBIR) PROGRAM**

**FINAL REPORT OF PHASE I STUDY**

TOPIC NUMBER: A95-106

PROPOSAL TITLE: Radiofrequency Plasma Ionization/Time-of-flight Mass Spectrometer for Real-time Monitoring of Trace Chemical Vapors During OB/OD Operations

CONTRACT NUMBER: DAAD09-96-C-0005

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## **SUMMARY**

A great need exists for a real-time analytical technique to monitor trace vapor emissions during open burning/open detonation (OB/OD) testing in BangBox facilities. In Phase I of this study, a corona discharge atmospheric pressure ionization/time-of-flight mass spectrometer (CDAPI/TOFMS) was successfully developed and evaluated for analyzing permanent gas, volatile organic, semi-volatile organic, and toxic metal target analytes selected from previous OB/OD tests [1,2]. Mass spectra illustrating selectivities were obtained. Sensitivities in the **parts-per-trillion** range and calibration curves were determined for various analytes. The CDAPI/TOFMS was shown to be more sensitive than GC/MS, SFC/MS, and FTIR. A detailed design of a prototype CDAPI/TOFMS for construction and testing during Phase II of this project is included in this report. The new design emphasizes improved instrument performance and facilitates instrument manufacturing and commercialization. **All Phase I objectives were accomplished.**

## **1. INTRODUCTION**

Conventionally, the destruction of obsolete explosives, propellants, and pyrotechnics by the Department of Defense has been performed by open burning/open detonation (OB/OD) processes [1,2]. Although OB/OD operations in isolated military bases would appear quite harmless, these operations have come under the scrutiny of federal and state environmental regulatory agencies. In compliance with the regulatory agencies, the U.S. Army has begun characterizing OB/OD emissions.

Currently, at Dugway Proving Ground, testing is centered around the BangBox, a 25-foot high fabric hemisphere inflated by a fan. Small-scale (up to ½ lb of detonable material or 5 lbs of combustible material) OB/OD experiments are conducted in the BangBox. Emission samples are collected in electropolished stainless steel canisters, on specially cleaned adsorbent polymer resin beads, and on ultra high purity quartz fiber filters. Samples are transported to analytical laboratories, where they are analyzed for specific target analytes.

There is a very great need for a real-time analytical instrument to monitor OB/OD emissions during BangBox tests. Sensor's Phase I proposal was to develop and test an atmospheric pressure radiofrequency plasma ionization (RPI)/ time-of-flight mass spectrometer (TOFMS) for real-time monitoring of trace chemical vapors during OB/OD operations. The specific Phase I objectives of this project were as follows:

(1) To construct and evaluate a prototype RPI source for producing ions for mass spectrometric detection from various OB/OD target analytes.

(2) To analyze representative target analytes chosen from previous OB/OD tests with an experimental TOFMS system to determine the sensitivities and selectivities of the system.

(3) To produce a detailed design of a prototype TOFMS system to be constructed and tested during Phase II of the project. The new mass spectrometer system will be used to monitor vapor emissions during OB/OD operations at the Dugway BangBox.

**All objectives of the Phase I proposal were accomplished.** The results of Phase I testing are described below.

## 2. EXPERIMENTAL AND RESULTS

### 2.1 Assembly and description of the mass spectrometer

The mass spectrometer was assembled as illustrated in Figure 1. An exploded view of the instrument is shown in Figure 2. Ions are formed at atmospheric pressure, and ions and neutral molecules enter the first vacuum region (approximately 0.1 torr) of the mass spectrometer by dynamic gas flow through the nozzle aperture (100  $\mu\text{m}$ ). As the gas flows through the orifice, many collisions take place among the ions and the molecules (provided that the diameter of the orifice is larger than the mean free path of the ions and molecules). The faster ions are decelerated and the slower ions are accelerated, due to the collisions, until all ions are moving in the same direction at the same velocity. This is a supersonic ion beam. The nozzle is posi-

tively charged for positive ions and negatively charged for negative ions to form a tightly collimated ion beam. A skimmer is placed in the supersonic ion beam, following the nozzle, to skim off the neutral molecules. The ion beam continues through the skimmer orifice (500  $\mu\text{m}$ ) into the second vacuum region (approximately  $10^{-4}$  torr) while most of the neutral molecules are removed by the vacuum pump. The skimmer also carries a positive potential for positive ions and a negative potential for negative ions to collimate the ion beam further. Following the skimmer, the ion beam is focused by the lenses before the ions flow into the third vacuum region (approximately  $10^{-6}$  torr). The pulsed repeller electrostatically deflects packets of ions up the flight tube; which is arranged perpendicularly with respect to the ion beam passing through the nozzle, skimmer, and lenses. The focus grid prevents stray ions (ions that are not repelled by the repeller) from entering the flight tube, reducing background noise. The grids on both ends of the flight tube isolate the flight tube from electrostatic fields. The ions travel to the detector at the end of the flight tube, lighter ions arriving before heavier ions, where they are detected.

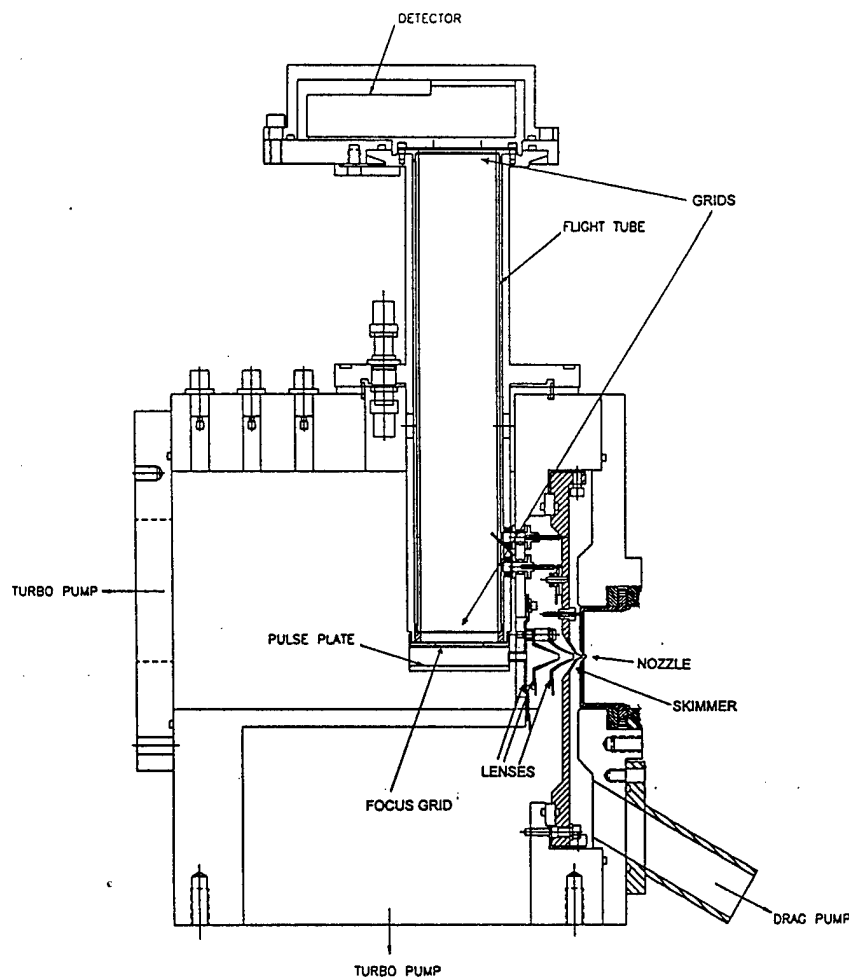


Figure 1. TOFMS.

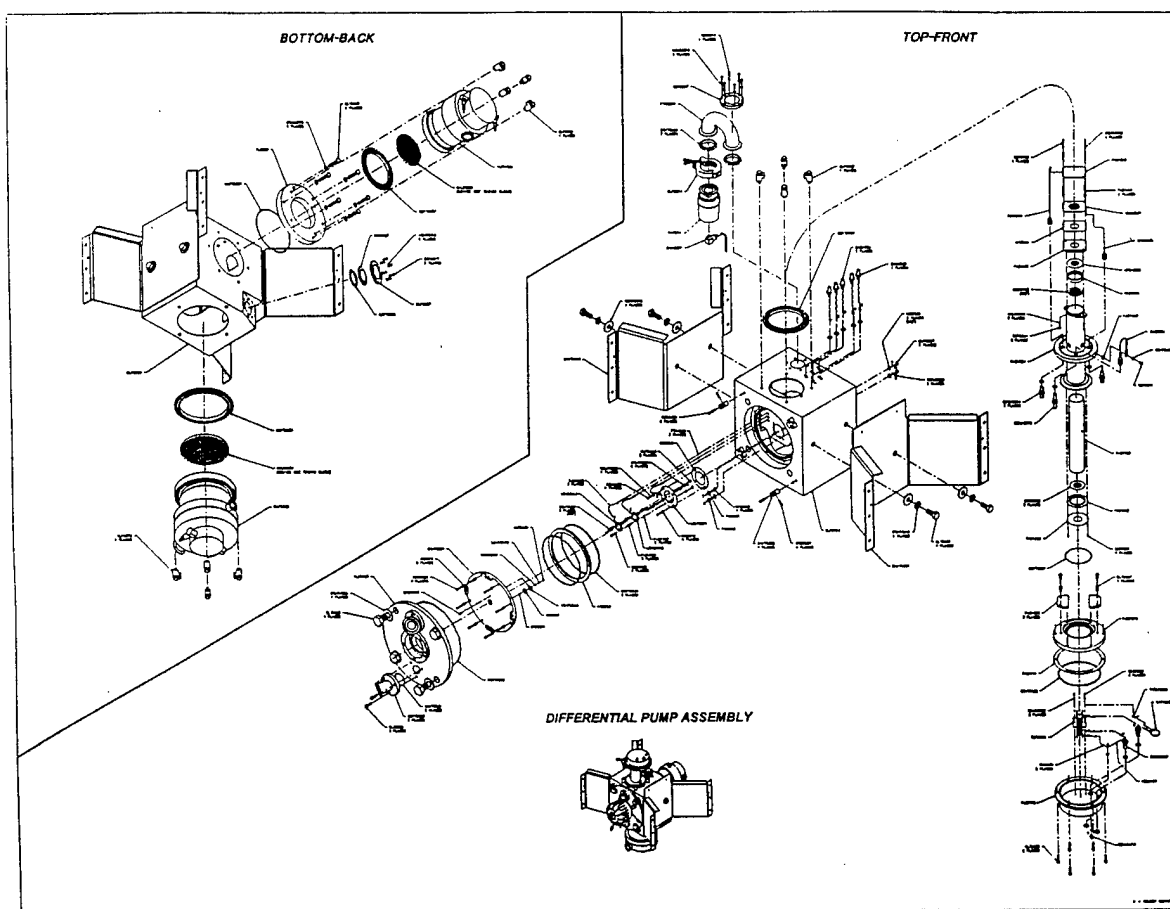


Figure 2. Exploded view of the TOFMS.

## 2.2 Design and testing of the ionization source

The RPI source (Figure 3) was designed, constructed, and coupled to the TOFMS, as described in the Phase I proposal. A fused silica discharge tube (1 mm id. x 6 mm o.d. x 7.5 cm) to contain the plasma was sealed to the TOFMS inlet. Helium, the plasma gas, was supplied to the discharge tube at flows that varied from 20 to 75 mL/min. Higher flow rates overworked the vacuum system. The RPI source was tuned to the appropriate frequency (320 kHz) to generate a plasma inside the discharge tube. The radiofrequency (RF) power levels were varied from 10 to 20 watts. Power settings higher than 20 watts could cause the power to reflect back to the power supply and damage it.

Because the discharge tube was sealed to the mass analyzer inlet, all ions produced by the RPI source entered the TOFMS, yielding a very intense background mass spectrum of the plasma gas. The intense background spectrum produced a noisy baseline, sometimes causing spectral interference between plasma gas and analyte peaks. These undesirable characteristics lowered the signal-to-noise ratio and greatly decreased the ability of the system to detect minute quantities of analytes. Increasing the RF power and helium flow to the plasma increased the background signal and tended to depress the analyte signals further.

Although the RPI/TOFMS is very versatile and capable of producing a range of ionization conditions, several weeks of experimentation revealed that there is no advantage to using the RPI source over the more conventional corona discharge atmospheric pressure ionization (CDAPI) source, due to the high spectral background level produced by the RPI source. In contrast to ionization in the RPI source, which occurs by both thermodynamically and kinetically controlled processes, ionization by the CDAPI is a thermodynamically controlled process (charge exchange, proton transfer) with a reagent ion. The RPI plasma has a large, hot ionization region. On the other hand, the CDAPI plasma has a small reaction region. Ions produced in the RPI plasma are not as thermally stable as, and are more prone to fragment than, ions produced by the corona discharge.

The CDAPI source, when maintained dry at 10 parts-per-billion (ppb) water or lower, ionized OB/OD target analytes as efficiently as the RPI source without the high spectral background. Thus, with the CDAPI source, analyte peaks with much better signal-to-noise ratios are produced. Furthermore, the CDAPI source is more easily controlled, is more easily electrically insulated, requires a simpler power supply, and is less hazardous than the RPI source. Figure 4 is a diagram of the mass spectrometer with the CDAPI source.

### 2.3 Preliminary evaluation of the CDAPI/TOFMS system for monitoring OB/OD vapor emissions

The performance of the TOFMS equipped with a CDAPI source was evaluated with target analytes studied in the BangBox series of tests. Representative compounds were selected from four classes of analytes: permanent gases, volatile organic compounds (VOCs), semi-volatile organic compounds (SVOCs), and toxic metals. Table 1 summarizes the results of the CDAPI/TOFMS performance evaluation.

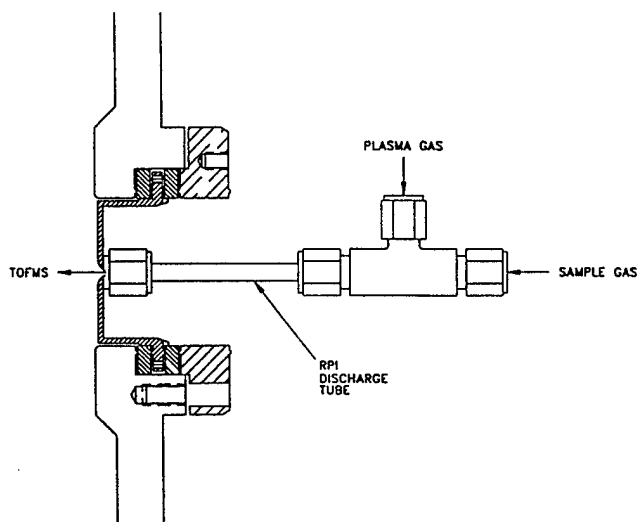


Figure 3. RPI ionization source.

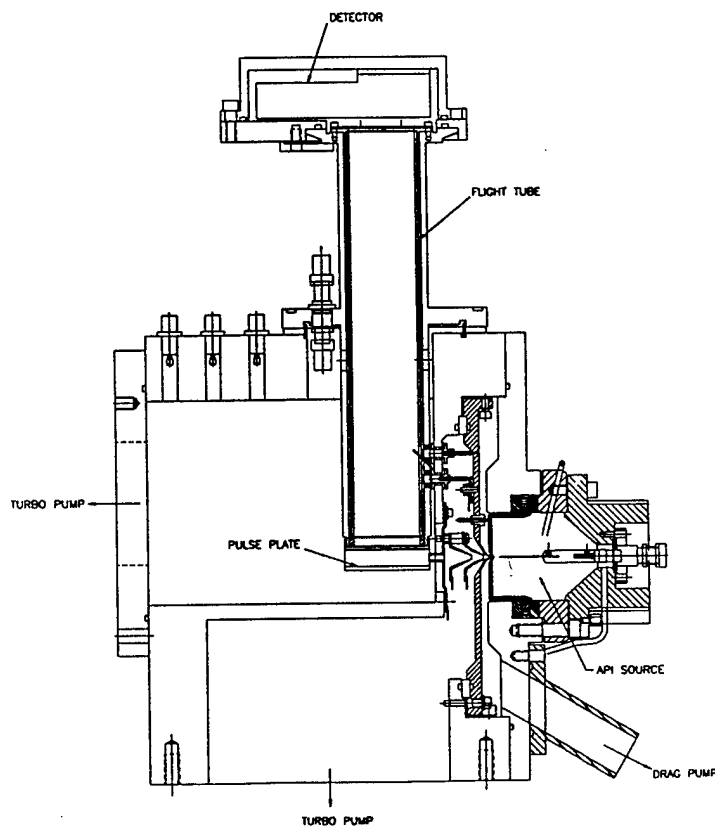


Figure 4. TOFMS with the CDAPI source.

**Table 1**  
*Results of the TOFMS Performance Evaluation*

Analytes tested	Results
<b>Permanent gases</b>	
CH <sub>4</sub> , H <sub>2</sub> O, O <sub>2</sub> , CO <sub>2</sub>	<ol style="list-style-type: none"> <li>1. Analytes detected</li> <li>2. Calibration curves obtained</li> <li>3. MDLs (&lt;50 ppt mole ratio in gas) established</li> </ol>
NO <sub>2</sub> , SO <sub>2</sub>	<ol style="list-style-type: none"> <li>1. Spectra of N<sub>2</sub>-H<sub>2</sub>O adduct ions interfered with detection</li> </ol>
<b>Volatile organic compounds</b>	
Benzene, vinyl chloride	<ol style="list-style-type: none"> <li>1. Analytes detected</li> <li>2. Calibration curves obtained</li> <li>3. MDLs (300 ppt mole ratio in gas) established</li> </ol>
<b>Semi-volatile organic compounds</b>	
2-Nitronaphthalene, 2,4-dinitrotoluene, pyrene, benz[a]anthracene	<ol style="list-style-type: none"> <li>1. Analytes detected</li> </ol>
2,4,6-Trinitrotoluene	<ol style="list-style-type: none"> <li>1. Analyte detected</li> <li>2. Calibration curve obtained</li> <li>3. MDL (50 ppt mole ratio in gas) established</li> </ol>
<b>Toxic metals</b>	
Mercury	<ol style="list-style-type: none"> <li>1. Analyte detected</li> <li>2. MDL (300 ppt mole ratio in gas) established</li> </ol>

### 2.3.1 Monitoring of permanent gases with the CDAPI/TOFMS

Figure 5 is a schematic diagram of the gas handling system used to prepare specific concentrations of the permanent gases in nitrogen (N<sub>2</sub>) prior to introduction into the CDAPI/TOFMS. Samples were diluted for instrument calibration and sensitivity measurements.

Several mixtures ranging from approximately 200 parts-per-trillion (ppt) to approximately 2 ppb of methane (CH<sub>4</sub>), water (H<sub>2</sub>O), oxygen (O<sub>2</sub>), and carbon dioxide (CO<sub>2</sub>) in high purity N<sub>2</sub> were prepared to calibrate the instrument (Tables 2 to 5). In Figure 6 is a typical mass spectrum showing traces of CH<sub>4</sub>, H<sub>2</sub>O, O<sub>2</sub>, and CO<sub>2</sub> in N<sub>2</sub>. The parameter settings are shown in Table 6. Figures 7 to 10 are calibration plots for the four gases, respectively, exhibiting three decades of linearity. The minimal detectable level (MDL) for each analyte is below 50 ppt. The MDLs are limited by the purity of the N<sub>2</sub> gas in which the analytes are detected, not by instrument performance. If N<sub>2</sub> of higher purity were available, the MDLs would drop.

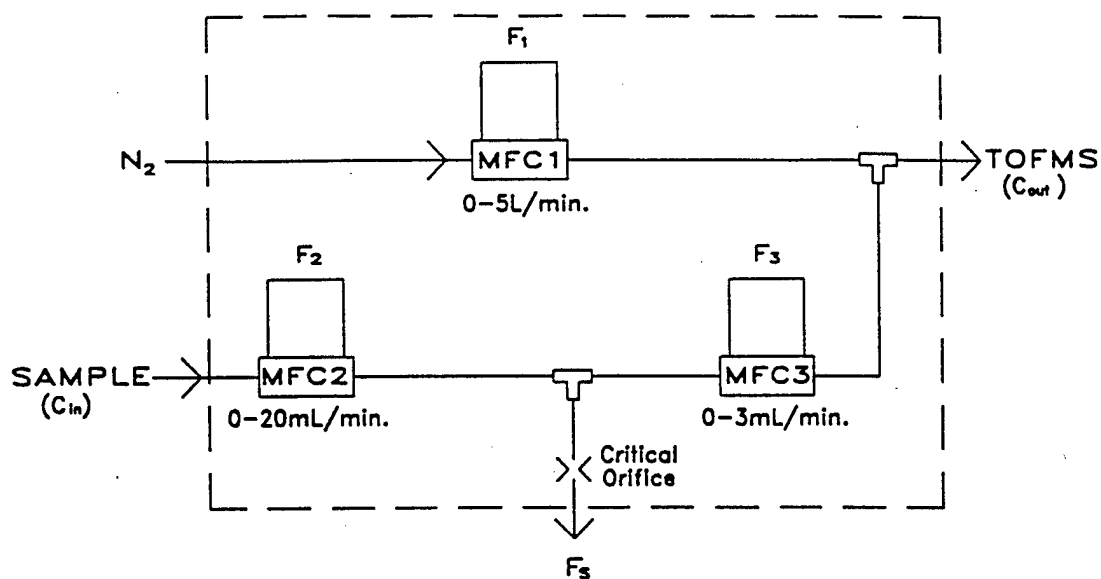


Figure 5. Schematic diagram of the gas handling system.

**Table 2**  
*Methane Calibration Data*

Signal ( $\mu V$ )	Concentration (ppb)
41.4	2.65
19.5	1.06
13.0	0.53
8.6	0.26
0.6	0.00
0.8	0.00
7.7	0.26
10.1	0.53
17.7	1.06
39.4	2.65
39.4	2.65
20.4	1.06
11.6	0.53
9.1	0.26
0.7	0.00

**Table 3**  
*Water Calibration Data*

Signal ( $\mu V$ )	Concentration (ppb)
1850	2.60
970	1.04
658	0.52
483	0.26
145	0.00
131	0.00
495	0.26
482	0.52
660	1.04
1935	2.60
2149	2.60
982	1.04
627	0.52
468	0.26
141	0.00

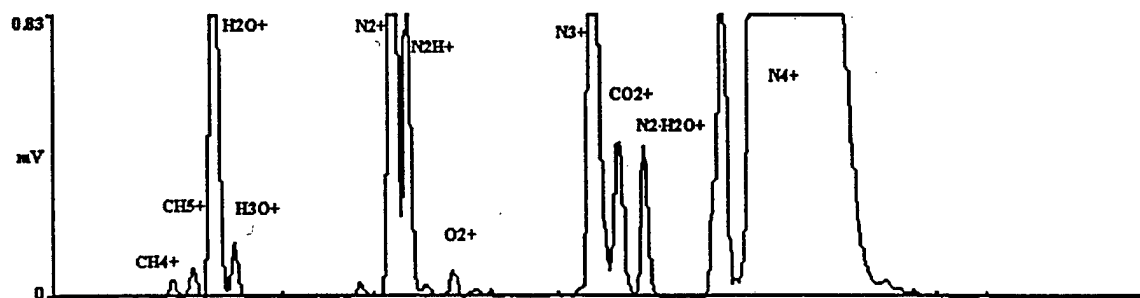


**Table 4**  
*Oxygen Calibration Data*

Signal ( $\mu\text{V}$ )	Concentration (ppb)
18.3	2.55
9.1	1.02
6.3	0.51
4.8	0.26
3.2	0.00
3.3	0.00
4.9	0.26
6.2	0.51
8.2	1.02
17.6	2.55
19.4	2.55
10.2	1.02
6.4	0.51
5.6	0.26
2.6	0.00

**Table 5**  
*Carbon Dioxide Calibration Data*

Signal ( $\mu\text{V}$ )	Concentration (ppb)
267	2.19
122	0.88
79	0.44
60	0.22
37	0.00
32	0.00
64	0.22
74	0.44
108	0.88
265	2.19
259	2.19
115	0.88
80	0.44
62	0.22
35	0.00



**Figure 6.** *A typical mass spectrum of high purity nitrogen.*

A certified calibration mixture of nitrogen dioxide ( $\text{NO}_2$ ) and sulfur dioxide ( $\text{SO}_2$ ) in air was analyzed with the CDAPI/TOFMS. Normally, calibration mixtures prepared in air contain at least 10 ppm of  $\text{H}_2\text{O}$ . Therefore, when  $\text{H}_2\text{O}$  from the cylinder was introduced into the nitrogen-based corona discharge ion source, the  $\text{H}_2\text{O}$  and  $\text{N}_2$  formed the nitrogen-water adduct ions  $\text{N}_2\cdot\text{H}_2\text{O}^+$ , mass 46, and  $\text{N}_2\cdot(\text{H}_2\text{O})_2^+$ , mass 64. The nitrogen-water adducts interfered with the determinations of  $\text{NO}_2$ , mass 46, and  $\text{SO}_2$ , mass 64. Modifications to the instrument system to eliminate or minimize these interferences will be detailed in Section 2.4.

**Table 6**  
*Instrument Control and Gas Blending Parameters and Settings for  
Analyzing Impurities in High Purity Nitrogen (Figure 6).*

Parameter	Setting	Parameter	Setting
<b>Instrument Control</b>		<b>Gas Blending</b>	
Ion mode	Positive	Bulk gas	Purified Nitrogen
Discharge current	0.60 $\mu$ A	Bulk gas MFC	Open
Discharge voltage	1993 V	Bulk gas flow	2000 mL/min
Nozzle	22.0 V	Calibration gas MFC	Closed
Skimmer	2.10 V	Calibration gas flow	1.00 mL/min
Lens 1	-30.0 V	Permeation tube MFC	Closed
Lens 2	-400 V	Permeation tube flow	0.00 mL/min
Lens 3	-50.0 V	Gas blending temperature	25°C
Pulser voltage	300 V		
Pulser frequency	3.0 kHz		
Pulse width	1.0 $\mu$ sec		
Focus grid	0.15 V		
Flight tube	-1470 V		
Detector	-2100 V		
API temperature	90°C		
Vacuum	8.2 x 10 <sup>-6</sup> mbar		
Spectra averaged	16384		

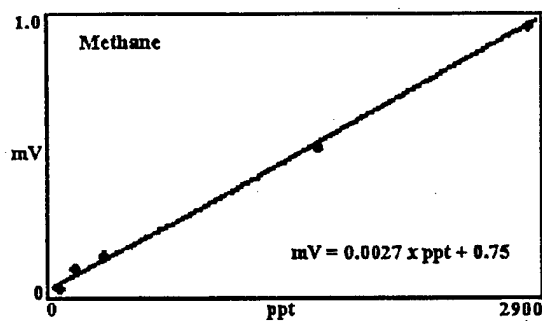


Figure 7. Methane calibration plot.

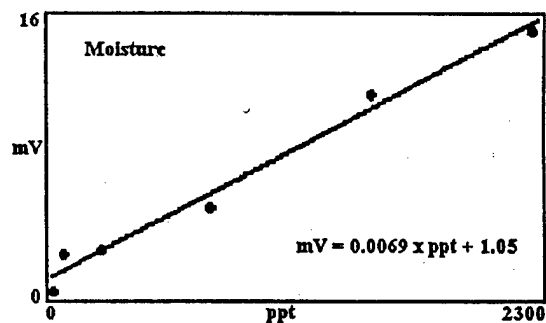


Figure 8. Water calibration plot.

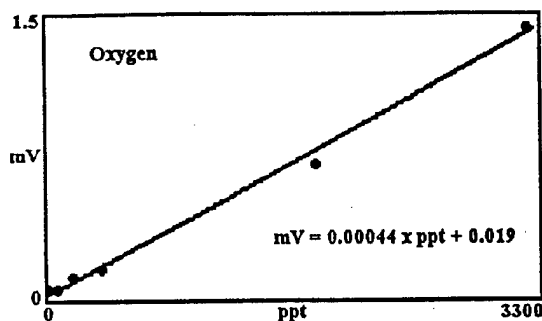


Figure 9. Oxygen calibration plot.

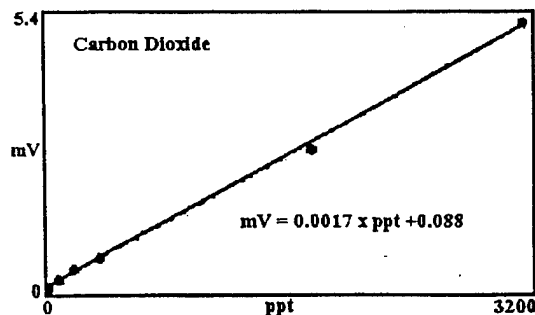


Figure 10. Carbon dioxide calibration plot.

### 2.3.2 Monitoring of VOCs with the CDAPI/TOFMS

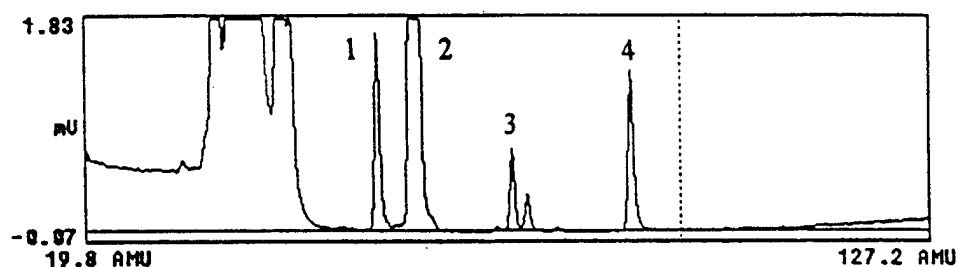


Figure 11. Mass spectrum of (4) benzene and (3) vinyl chloride. Other peaks: (1)  $N(H_2O)_2^+$ , (2)  $N_4^+$ .

**Table 7**  
*Instrument Control and Gas Blending Parameters and Settings for  
Analyzing VOCs in Air (Figure 11).*

Parameter	Setting	Parameter	Setting
<b>Instrument Control</b>		<b>Gas Blending</b>	
Ion mode	Positive	Bulk gas	Purified Nitrogen
Discharge current	0.80 $\mu$ A	Bulk gas MFC	Open
Discharge voltage	2406 V	Bulk gas flow	2000 mL/min
Nozzle	17.0 V	Calibration gas MFC	Open
Skimmer	1.20 V	Calibration gas flow	3.50 mL/min
Lens 1	-28.0 V	Permeation tube MFC	Closed
Lens 2	-300 V	Permeation tube flow	0.00 mL/min
Lens 3	-50.0 V	Gas blending temperature	25°C
Pulser voltage	300 V		
Pulser frequency	3.0 kHz		
Pulse width	1.8 $\mu$ sec		
Focus grid	0.15 V		
Flight tube	-1470 V		
Detector	-1900 V		
API temperature	90°C		
Vacuum	$8.2 \times 10^{-6}$ mbar		
Spectra averaged	2048		

A certified calibration mixture of benzene and vinyl chloride, both at 50 ppm, in air was introduced into the CDAPI/TOFMS through the gas handling system (Figure 5). A typical mass spectrum is shown in Figure 11. Table 7 lists the parameter settings used to obtain the mass spectrum. Several dilutions of the calibration mixture in high purity N<sub>2</sub> were prepared with the gas handling system and introduced into the CDAPI/TOFMS to produce the target analyte calibration curves (Figures 12 and 13 and Tables 8 and 9, respectively). The MDL for each analyte was 300 ppt. The new CDAPI/TOFMS prototype design, discussed in Section 2.4, will greatly improve the MDLs.

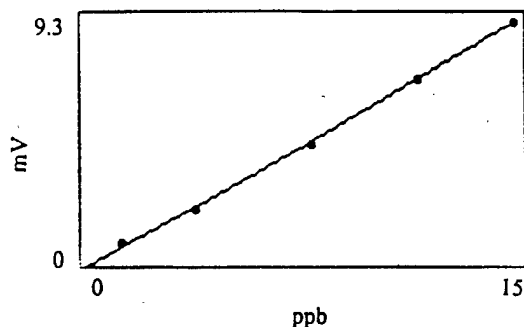


Figure 12. Benzene calibration plot.

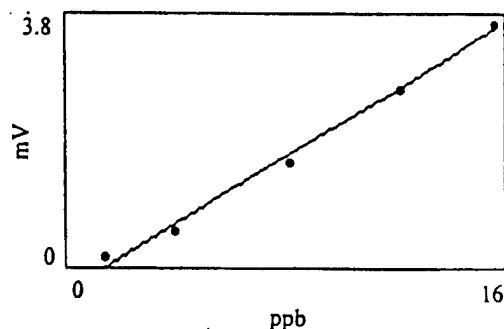


Figure 11. Vinyl chloride calibration plot.

**Table 8**  
*Benzene Calibration Data*

Signal (mV)	Concentration (ppb)
9.27	15.4
7.11	12.0
4.63	8.05
2.11	3.94
0.77	1.45

**Table 9**  
*Vinyl Chloride Calibration Data*

Signal (mV)	Concentration (ppb)
3.77	15.6
2.75	12.1
1.59	8.13
0.53	3.98
0.12	1.46

### 2.3.3 Monitoring of SVOCs with the CDAPI/TOFMS

Gaseous calibration mixtures containing the permanent gases and various VOCs can be obtained without much difficulty. However, because of the relatively low volatilities of the SVOCs, calibration mixtures of those compounds in the vapor state are neither readily available nor reliable. In order to introduce well-defined quantities of the SVOC target analytes into the CDAPI/TOFMS, a system with a special solid phase injector (Figure 14) was built. The injector consists of a platinum wire sealed inside of a stainless steel chamber. To load the injector, the wire is removed from the steel chamber (Figure 15A), a drop of solution containing the analyte(s) of interest is deposited on the wire, and the solvent is allowed to evaporate. To introduce sample into the instrument, the wire is re-inserted into the steel chamber and the analytes are desorbed from the wire and carried into the ion source by a stream of heated N<sub>2</sub> (Figure 15B). Figure 16 shows a mass spectrum of four target analytes: 2-nitronaphthalene; 2,6-dinitrotoluene; pyrene; and benz[*a*]anthracene (approximately 15

ppb with respect to each analyte in the gas stream carrying the vapor). Table 10 lists the parameter settings under which the mass spectrum was obtained. Figure 17 is a typical mass spectrum of 2,4,6-trinitrotoluene (TNT) and Table 11 lists the parameter settings. Figure 18 is the calibration curve for TNT and Table 12 is the calibration data. The MDL for TNT is 50 ppt.

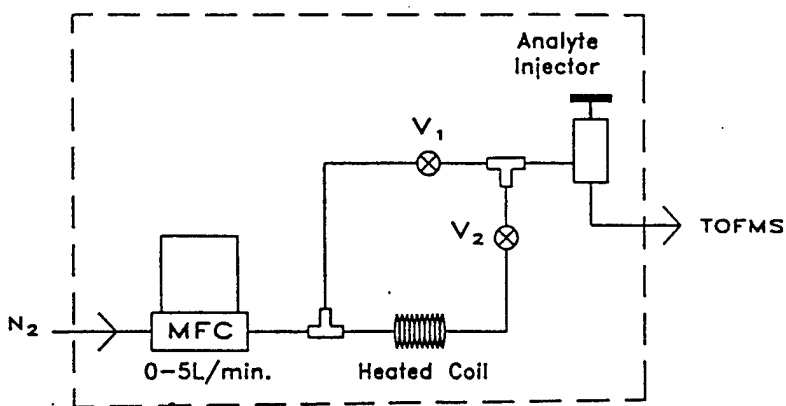


Figure 14. SVOC target analyte introduction system.

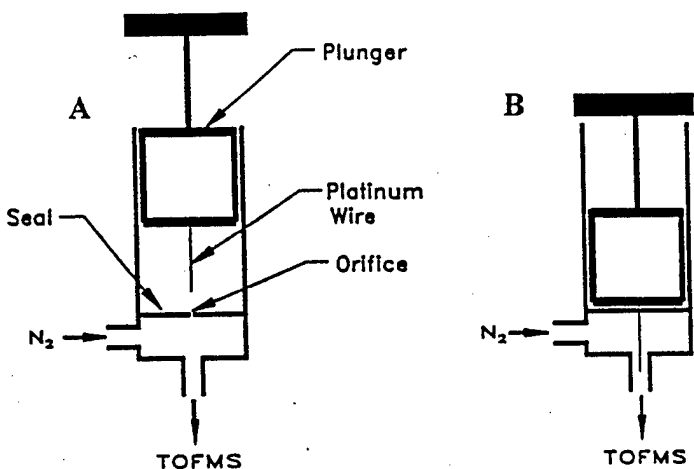


Figure 15. SVOC target analyte solid phase injector with the platinum wire in the sample load position (A) and in the sample injection position (B).

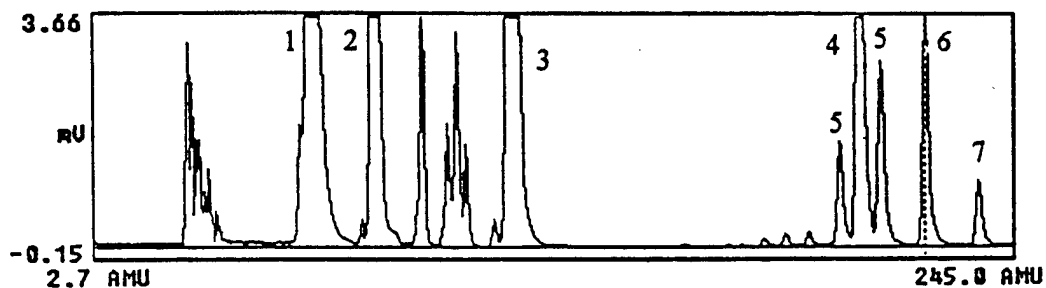
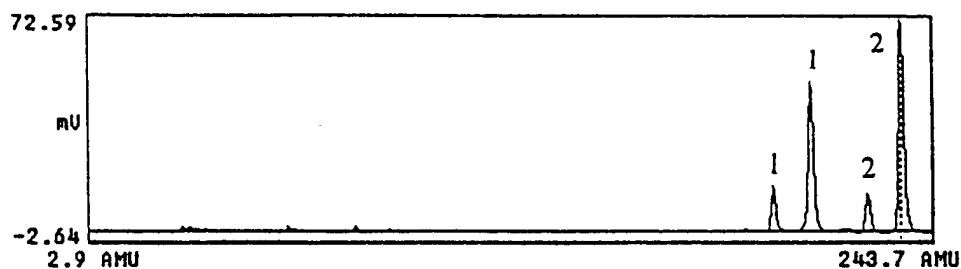


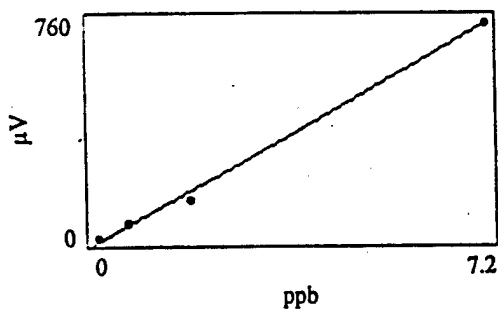
Figure 16. Mass spectrum of (4) 2-nitronaphthalene, (5) 2,6-dinitrotoluene, (6) pyrene, (7) benz[a]anthracene. Other peaks: (1)  $H_2O^+$ , (2)  $N_2^+$ , (3)  $N_4^+$ .

**Table 10**  
*Instrument Control and Gas Blending Parameters and Settings for  
Analyzing SVOCs (Figure 16).*

Parameter	Setting	Parameter	Setting
<b>Instrument Control</b>		<b>Gas Blending</b>	
Ion mode	Positive	Bulk gas	Purified Nitrogen
Discharge current	1.00 $\mu$ A	Bulk gas MFC	Open
Discharge voltage	2379 V	Bulk gas flow	4000 mL/min
Nozzle	18.0 V	Calibration gas MFC	Closed
Skimmer	3.00 V	Calibration gas flow	0.00 mL/min
Lens 1	-30.0 V	Permeation tube MFC	Closed
Lens 2	-300 V	Permeation tube flow	0.00 mL/min
Lens 3	-50.0 V		
Pulser voltage	300 V	<b>Sample Injection</b>	
Pulser frequency	2.5 kHz	Temperature	250°C
Pulse width	1.2 $\mu$ sec	Carrier gas flow	4000 mL/min
Focus grid	0.15 V		
Flight tube	-1900 V		
Detector	-2100 V		
API temperature	90°C		
Vacuum	4.5 x 10 <sup>-6</sup> mbar		
Spectra averaged	16384		



**Figure 17.** Mass spectrum of (2) 2,4,6-trinitrotoluene. Other peaks: (1) 2,6-dinitrotoluene.



**Figure 18.** Trinitrotoluene calibration plot.

**Table 11**  
*Instrument Control and Gas Blending Parameters and Settings for  
 Analyzing TNT (Figure 17).*

Parameter	Setting	Parameter	Setting
<b>Instrument Control</b>		<b>Gas Blending</b>	
Ion mode	Positive	Bulk gas	Purified Nitrogen
Discharge current	1.50 $\mu$ A	Bulk gas MFC	Open
Discharge voltage	2196 V	Bulk gas flow	4000 mL/min
Nozzle	17.0 V	Calibration gas MFC	Closed
Skimmer	1.00 V	Calibration gas flow	0.00 mL/min
Lens 1	-30.0 V	Permeation tube MFC	Closed
Lens 2	-300 V	Permeation tube flow	0.00 mL/min
Lens 3	-50.0 V		
Pulser voltage	300 V	<b>Sample Injection</b>	
Pulser frequency	3.0 kHz	Temperature	250°C
Pulse width	1.3 $\mu$ sec	Carrier gas flow	4000 mL/min
Focus grid	0.25 V		
Flight tube	-1900 V		
Detector	-2100 V		
API temperature	90°C		
Vacuum	4.5 x 10 <sup>-6</sup> mbar		
Spectra averaged	2048		

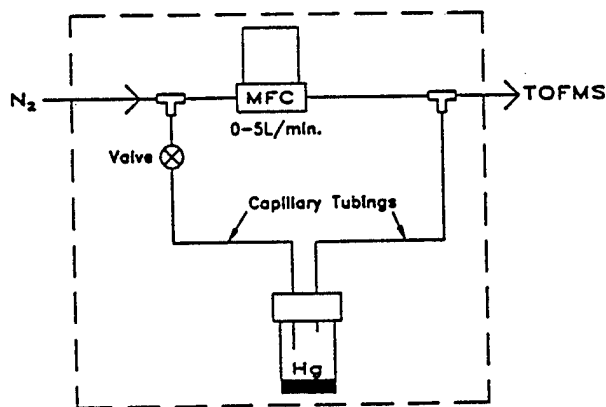
**Table 12**  
*2,4,6-Trinitrotoluene Calibration Data*

Signal ( $\mu$ V)	Concentration (ppb)
20	.18
70	.72
150	1.80
760	7.20

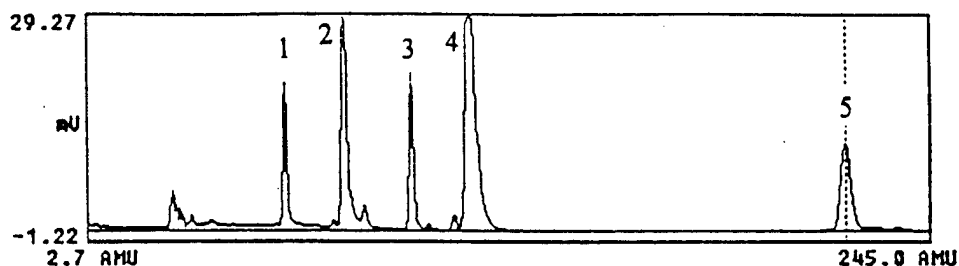
### 2.3.4 Monitoring of mercury

The system illustrated schematically in Figure 19 was used to introduce mercury vapors into the mass spectrometer. A mass spectrum of mercury, approximately 45 ppb, and is shown in Figure 20 and the parameter settings are listed in Table 13. The MDL was

300 ppt. Experimentation clearly indicates that it is possible to determine trace amounts of mercury with the CDAPI/TOFMS.



**Figure 19.** *Mercury vapor sample introduction system.*



**Figure 20.** Mass spectrum of (5) mercury. Other peaks: (1)  $H_2O^+$ , (2)  $N_2^+$ , (3)  $N_3^+$ , (4)  $N_4^+$ .

#### 2.4 Comparison of the CDAPI/TOFMS to other types of analytical instrumentation.

Conventionally, during BangBox testing, VOCs are trapped in highly polished stainless steel canisters or on solvent-extracted polymer resins and transported to the laboratory for analysis days later [1,2]. Canister samples are concentrated and then introduced into a GC/quadrupole mass spectrometer (GC/MS). SVOCs are collected on very high purity quartz fiber filters and transported to the laboratory, where they are extracted with solvents and analyzed by GC/MS and supercritical fluid chromatograph/selected ion monitoring/MS (SFC/SIM/MS) [1,2]. Typically, the GC/MS and SFC/SIM/MS sample collection and analysis methods are capable of detecting analytes at ppm and ppb (mole ratio) concentrations in the BangBox air, respectively. For example, TNT at 3 to 30 ppm (mole ratio) in the BangBox air can be detected in samples collected for and analyzed by GC/MS. Similarly, TNT at 100 ppb in BangBox air can be detected in samples collected for and analyzed by SFC/SIM/MS. Concentrations of target analytes in BangBox air were calculated from results reported in references 1 and 2.

A Fourier transform infrared (FTIR) spectrometer under favorable conditions is capable of real-time analysis in relatively clean air at concentrations in the low ppm to high ppb range [3,4]. Particulate matter in the air causes significant loss in sensitivity. Since detonations and burns in the BangBox usually produce substantial quantities of particulates, it is questionable whether or not FTIR spectrometry is sensitive enough for this application.

**Table 14**  
*Comparison of Instrumental Analytical Techniques*

Instrument	MDL in Air	Real time	Limitation
GC/MS	Low ppm	No	Sample must be collected and concentrated or extracted
SFC/SIM/MS	High ppb	No	Sample must be collected and extracted
FTIR spectrometer	Low ppm to high ppb	Yes	Air must be particulate free
TOFMS	Low ppt	Yes	



The CDAPI/TOFMS is capable of measuring analytes in air in the ppt range. As stated above, permanent gases were detected at 50 ppt, benzene and vinyl chloride at 300 ppt, TNT at 50 ppt and mercury at 300 ppt. With the new instrument design described below, the MDLs are expected to improve significantly.

The information in this section is summarized in Table 14.

## 2.5 Design of a new prototype CDAPI/TOFMS for OB/OD testing at the BangBox during Phase II

The new prototype CDAPI/TOFMS instrument design incorporates ideas to improve performance, selectivity, and sensitivity. While MDLs reported above are already noteworthy, the new CDAPI/TOFMS prototype design for Phase II testing will significantly improve MDLs. This new instrument is also designed in anticipation of construction methods that will greatly facilitate instrument manufacture and commercialization.

The CDAPI source is depicted in Figure 21. It has been shown to be very effective for ionizing OB/OD target analytes, providing the source is dry (less than 10 ppb  $\text{H}_2\text{O}$ ). Therefore membrane sample introduction will be utilized to prevent contamination of the ion source with  $\text{H}_2\text{O}$  and particulates. Sample vapors flow continuously through the gas inlet into the ionization chamber and out through the gas outlet, creating a dynamic gas stream which can be sampled for analysis. High electrical potential is applied to the discharge needle, by way of the electrical feedthrough, creating a corona discharge plasma between the needle point and the nozzle. The plasma ionizes the  $\text{N}_2$  carrier gas in the chamber, which transfers charge to the analyte molecules.

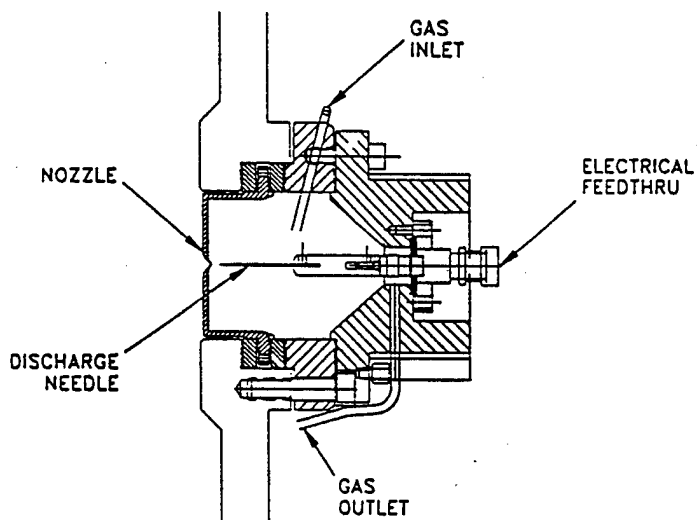


Figure 21. CDAPI source.

Newly formed ions are pulled through an orifice at the tip of the nozzle into the ion beam expansion and focusing region of the instrument (Figure 22). The ion beam undergoes a supersonic expansion, which equalizes the kinetic energies of all of the ions in the beam. In this region, instead of focusing the ion beam with electrostatically charged rings, as was done in Phase I, it will be focused with RF quadrupoles, resulting in a much tighter ion beam. The constricted ion beam will improve resolution and reduce possible interference and background noise.

The ion beam flows past a repeller (pulse) plate where packets of the beam are repelled up the flight tube. To better match the profile of the repelled ion packets, the flight tube has a rectangular cross-section rather than the conventional circular cross-section. Also, instead of enclosing a field-free flight path (as in the Phase I instrument), the flight tube envelopes a zone to which an electrical field is applied. The profile of the applied field is designed to improve the mass resolution and signal-to-noise ratio by minimizing the dependence of the ion flight times on the initial start positions of

the ions. The net effect is more compact ion packets at the flight tube exit, translating into a narrower signal per packet with greater intensity. This will decrease possible interference and background noise.

Exiting the flight tube, the ions collide against a large area collector. The collector is larger than those in conventional detector designs to increase ion collection efficiency. The new type of ion detector geometry and detection electronic system (to be patented) combine the best features of a transient digitizer (waveform recorder) with those of a time-to-digital converter to greatly improve the signal-to-noise ratio, dynamic range, and time resolution.

### 3. CONCLUSIONS

The CDAPI/TOFMS is capable of analyzing the various OB/OD target analytes (explosives, propellants, pyrotechnics, and their emissions). Some of the target analytes require that the ionization source be maintained dry (10 ppb water or lower) to achieve efficient ionization and to avoid chemical interferences. This can be accomplished by placing a semipermeable membrane at the mass spectrometer inlet. A membrane inlet can have an additional advantage. It would reduce maintenance downtime by excluding particulate contamination in the ionization source, and it would increase selectivity for the specific types of compounds of interest.

Representative permanent gas, VOC, SVOC, and toxic metal target analytes were successfully analyzed by the TOFMS. Analyte sensitivities are in the **parts-per-trillion** range.

The CDAPI/TOFMS is a real-time analyzer which is much more sensitive than GC/MS and SFC/MS, the more conventional non-real-time instruments used in the OB/OD testing program. The CDAPI/TOFMS is also much more sensitive than FTIR.

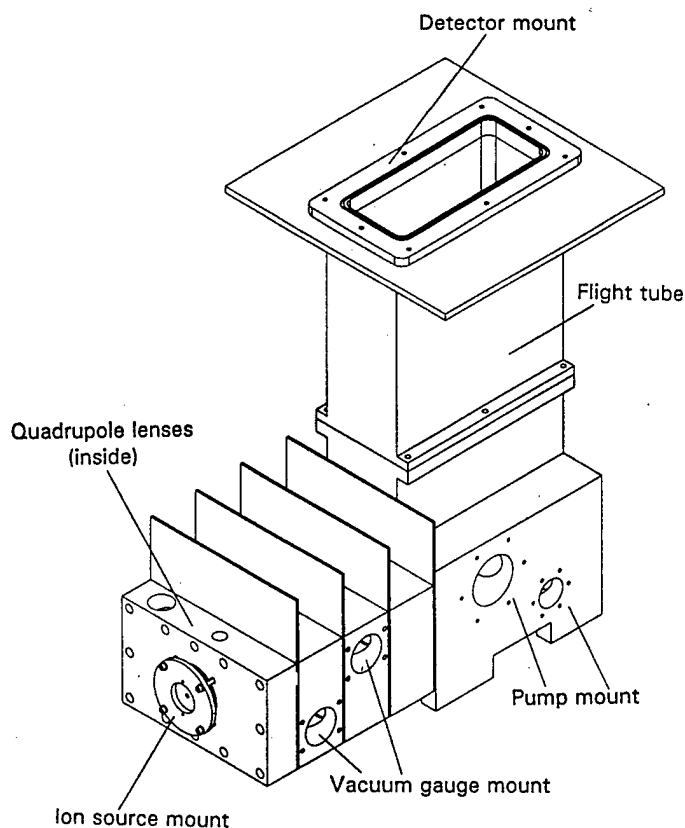


Figure 22. New TOFMS prototype.

#### 4. REFERENCES

1. M. Johnson, *Development of Methodology and Technology for Identifying and Quantifying Emission Products from Open Burning and Open Detonation Thermal Treatment Methods, BangBox Test Series*, Vols. 1-3, Final Report, U.S. Army Armament, Munitions and Chemical Command, January 1992.
2. M. Johnson, *Development of Methodology and Technology for Identifying and Quantifying Emission Products from Open Burning and Open Detonation Thermal Treatment Methods, Field Test Series A and B*, Vols. 1 and 2, Final Report, U.S. Army Armament, Munitions and Chemical Command, January 1992.
3. M.L. McKelvy, T.R. Britt, B.L. Davis, J.K. Gillie, L.A. Lentz, A. Leugers, R.A. Nyquist, C.L. Putzig, *Anal. Chem.*, **68**, 93R (1996).
4. H. Xiao, S.P. Levine, *Anal. Chem.*, **65**, 2262 (1993).